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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]A catalyst pattern used when this invention carries out the pyrolysis of the carbon-containing material and a carbon nanotube is compounded, and a formation method for the same, It is related with the manufacturing method of the carbon nanotube pattern to which the pyrolysis of the carbon-containing material is carried out under existence of a carbon nanotube pattern, a manufacturing method for the same, and this catalyst pattern.
[0002]
[Description of the Prior Art]How to carry out the pyrolysis of the carbon-containing material under existence of the substrate which has the catalyst particles for carbon nanotube composition on the surface, and to grow up a carbon nanotube on the substrate in order to compound a carbon nanotube [Chemical vapor deposition (CVD method)] is known. As a manufacturing method of the substrate in this case, detailed fine pores are made to a (i) substrate, and the method of forming a minute catalyst particle on a substrate by etching of the method of embedding a catalyst particle there and a (ii) metal plate, etc. are known. When using such a catalyst substrate, the carbon nanotube membrane got blocked vertically on the substrate and densely is obtained, but there is a problem that production of the substrate takes big difficulty.
[0003]
[Problem(s) to be Solved by the Invention]The catalyst pattern used when this invention carries out the pyrolysis of the carbon-containing material and a carbon nanotube is compounded, Let it be the technical problem to provide the formation method of the carbon nanotube pattern formed using this catalyst pattern, and this catalyst pattern, and the manufacturing method of the carbon nanotube pattern using this catalyst pattern.
[0004]

[Means for Solving the Problem]This invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. That is, according to this invention, a formation method of a catalyst pattern, a carbon nanotube pattern, and a catalyst pattern shown below and a formation method of a carbon nanotube pattern are provided.

(1) Are the catalyst pattern for carbon nanotube production formed in a base surface, and this catalyst pattern, A catalyst pattern for carbon nanotube production forming by removing these photosensitive materials included in this pattern from a pattern which consists of photosensitive materials beforehand formed on a base, and a mixture containing a catalyst.

(2) Are the catalyst pattern for carbon nanotube production formed in a base surface, and this catalyst pattern, While removing these photosensitive materials included in this pattern from a pattern which consists of photosensitive materials beforehand formed on a base, and a mixture containing a catalyst precursor, A catalyst pattern for carbon nanotube production forming by transforming a catalyst precursor contained in this pattern to a catalyst.

(3) The above (1) or (2) catalyst patterns for carbon nanotube production in which line width contains a catalyst small-gage wire of 10 micrometers or less in this catalyst pattern.

(4) One catalyst pattern for carbon nanotube production of aforementioned (1) - (3) in which this catalyst pattern contains catalyst support.

(5) The above (1) Carbon nanotube pattern forming along one catalyst pattern top for carbon nanotube production of - (4). (6) In a method of forming a catalyst pattern for carbon nanotube production in a base surface, (i) A process of applying coating liquid containing this catalyst and photosensitive materials on this base, and forming a photosensitive layer, (ii) A process exposed to pattern state at a photosensitive layer formed by this application process, (iii) A process of removing photosensitive materials included in this pattern from a pattern which consists of photosensitive materials obtained by process of developing a photosensitive layer exposed by this exposure process, and a (iv) this developing process, and a catalyst, a formation method of a catalyst pattern characterized by a thing, ** and others.

(7) A formation method of a catalyst pattern of the above (6) in which this coating liquid contains catalyst support.

(8) A formation method of a catalyst pattern of the above (6) performed by this coating liquid's containing a catalyst support precursor, and calcinating this photosensitive-materials removal process under an inert gas atmosphere or oxidizing gas atmosphere.

(9) In a method of forming a catalyst pattern for carbon nanotube production in a base surface, (i) A process of applying coating liquid containing a precursor and photosensitive materials of this catalyst on this base, and forming a photosensitive layer, (ii) A process exposed to pattern state at a photosensitive layer formed by this application process, (iii) From a pattern which consists of photosensitive materials obtained by process of developing a photosensitive layer

exposed by this exposure process, and a (iv) this developing process, and this catalyst precursor. A formation method of a process of removing photosensitive materials included in this pattern, a process of changing into a catalyst pattern a catalyst precursor pattern obtained by a (v) this photosensitive-materials removal process, and a catalyst pattern characterized by a thing, ** and others.

(10) A formation method of a catalyst pattern of the above (9) in which this coating liquid contains catalyst support.

(11) By this coating liquid's containing a catalyst support precursor, and calcinating a pattern which consists of photosensitive materials obtained by this developing process, and a catalyst precursor under an inert gas atmosphere, oxidizing gas atmosphere, or a reducing gas atmosphere, A formation method of a catalyst pattern of the above (9) which performs simultaneously this photosensitive-materials removal process and a converting process to a catalyst pattern of this catalyst precursor pattern.

(12) Said material which is the catalyst pattern material of construction for carbon nanotube production formed in a base surface, and is characterized by this material consisting of a pattern of photosensitive materials and a mixture containing a catalyst.

(13) Said material which is the catalyst pattern material of construction for carbon nanotube production formed in a base surface, and is characterized by this material consisting of a pattern of a mixture containing photosensitive materials and a catalyst precursor.

(14) One material of aforementioned (12) - (13) in which this pattern contains catalyst support or a catalyst support precursor.

(15) The above (1) Manufacturing method of a carbon nanotube pattern carrying out the pyrolysis of the carbon-containing material under existence of one catalyst pattern of - (4).

[0005]

[Embodiment of the Invention]The catalyst used by this invention is a catalyst which can be used when carrying out the pyrolysis of the carbon-containing material and compounding a carbon nanotube. As this catalyst, various kinds of publicly known things, usual, and a transition metal are used conventionally. Especially as this catalyst metal, the metal of a group VIII, for example, nickel, cobalt, molybdenum, Fe, Cu, V, Pd, etc. are mentioned from V. The catalyst used by this invention can be metal, and also they can be a metaled compound, for example, metallic boride, a metallic oxide, etc., and as long as it has a catalysis in composition of a carbon nanotube, what kind of thing may be sufficient as it.

[0006]The catalyst support used by this invention consists of porous material generally used conventionally. Alumina, silica, silica alumina, magnesia, zirconia, boria, zeolite, etc. are included by such catalyst support.

[0007]Although the catalyst precursor used by this invention is a soluble compound of the transition metal which gives said catalyst by chemical preparation, such as heating, oxidation,

reduction, soluble salts, such as the nitrate and a halogenide, organic acid salt, soluble organicity complex salt, etc. are usually used.

[0008]Although the catalyst support precursor used by this invention is a soluble compound of the metal which gives said catalyst support by chemical preparation, such as heating, oxidation, reduction, soluble salts, such as the nitrate and a halogenide, organic acid salt, soluble organicity complex salt, etc. are usually used.

[0009]When the coat is irradiated, a polymerization or the bridge-construction-ized thing of a negative mold is included for the thing and exposed part of the positive type which the exposed part disassembles by the photosensitive materials used by this invention.

[0010]As photosensitive materials (negative-mold material) which an exposed part hardens, various kinds of publicly known things are used conventionally. Generally it is the photosensitive materials containing epoxy groups (glycidyl group etc.), non-** groups (a vinyl group, a propenyl group, an acrylyl group, a methacryloyl group, a vinyl ether group, etc.), etc. as a reactant group, and it is as follows when the example is shown.

(i) Glycidyl methacrylate ethyl acrylate copolymer (ii) poly (glycidyl methacrylate)

(iii) The dry etching-proof [maleic acid methyl ester content methacrylic system polymers (iv)] nature negative-mold electron-beam-resist aforementioned photosensitive materials, Usually, the polymerization initiator which generates a radical by exposure for promoting a polymerization and bridge construction of the reactant group, a polymerization initiator, a sensitizer which generate a cation and an anion by exposure, etc. are contained.

[0011]As photodegradable photosensitive materials (positive type material) disassembled by exposure, various kinds of publicly known things are used conventionally. For example, it is as follows when the example is shown.

(i) Poly (methyl methacrylate)

(ii) Poly meta KURIAMIDO (iii) poly (alpha-cyano acrylic acid alkyl ester)

(iv) Poly (butene-1-sulfone)

(v) Methyl-methacrylate / acrylonitrile copolymer (vi) poly (methacrylic acid hexafluoro butylester)

(vii) Poly (methyl isopropenyl ketone)

[0012]As photosensitive materials (photosensitive resin composition etc.), very many things besides the aforementioned thing are proposed as a patent, and those things can be applied by this invention.

[0013]In one mode which manufactures the catalyst pattern of this invention, photosensitive materials and coating liquid including a catalyst are prepared. In this case, although it depends on the kind of those photosensitive materials for the solvent which dissolves or distributes photosensitive materials, an aqueous solvent and an organic solvent are used. Although the concentration in particular of the photosensitive materials in coating liquid is not restrained, 10-

1000 g/L is usually 100-500 g/L preferably. 10-500 g/L of catalyst concentration is usually 20-100 g/L preferably. The rate of a catalyst is a rate of one to 0. 5 weight section preferably 0.001 to 20 weight section per photosensitive-materials 100 weight section.

[0014]Distributing in a solvent the catalyst included in coating liquid by the shape of an ultrafine particle, the mean particle diameter is usually about 1-20 nm. Alcohol, ketone, ester, hydrocarbon, etc. are included as said organic solvent. As the example, for example Methanol, propyl alcohol, amyl alcohol, A hexanol, cyclohexanol, heptanol, octyl alcohol, cyclohexane, methyl ethyl ketone, a diethyl ketone, cycloheptane, n-hexane, n-heptane, isooctane, n-Deccan, benzene, toluene, xylene, etc. are mentioned. Use of the organic solvent which has the boiling point in the range which is 50-200 ** in this invention is preferred.

[0015]In order to prepare coating liquid preferably, catalytic liquid is made, it ranks second and this catalytic liquid is made to dissolve thru/or distribute photosensitive materials first in this invention. As a preparing method of catalytic liquid, what is necessary is just a method which may distribute a catalyst ultrafine particle uniformly in a solvent, and arbitrary methods can be used. A surface-active agent is added to an organic solvent, and it is made to dissolve in it first in the desirable preparing method. Next, the catalyst metallic compounds of fusibility are added to that organic solvent, and it is made to dissolve in it to the organic solvent containing this surface-active agent. Subsequently, the catalyst metallic compounds in this organic solvent are returned, and the microemulsion (catalytic liquid) containing a catalyst ultra-fine particle is obtained by making insoluble ultrafine particle-like catalyst metal generate.

[0016]as said surface-active agent -- an ionic surfactant -- a cationic surface-active agent and an anionic surface active agent are used preferably. In this case, as a cationic surface-active agent, the carbon numbers 8-22 and the quarternary ammonium salt which has the long chain alkyl group and alkenyl group of 12-20 preferably can be used. As an example of a cationic surface-active agent, a didecyl dimethylannmonium star's picture, Didecyl dimethylammoniumchloride, a didodecyl dimethylannmonium star's picture (or chloride), a Sept Iles trimethylammonium star's picture (or chloride), a dodecyl trimethylammonium star's picture (or chloride), etc. can be mentioned. Dioctylsulfo SASSHINETO sodium salt etc. are mentioned as an example of an anionic surface-active agent. The using rate of a surface-active agent is 7 to 15 % of the weight preferably one to 20% of the weight among a solution. As said soluble catalyst metallic compounds, the halogenides (a chloride, a bromide, etc.) of catalyst metal, organic acid salt (acetate etc.), organic complex salt (acetylacetonato, acetyl acetate, etc.), a nitrate, etc. are mentioned.

[0017]Although the method of using the chemical reducing agents using hydrogen gas as reduction for returning the catalyst metallic compounds which dissolve into a solution to insoluble metal, such as hydrazine and sodium borohydride besides reduction, is mentioned, use of a chemical reducing agent is preferred. The reduction method using this chemical

reducing agent is enforced in ordinary temperature more than 1 mol twice of the amount of theories, and by adding a twice as many 2-10-mol chemical reducing agent as this under stirring in a solution preferably. In this case, that chemical reducing agent can be added with the gestalt of solution or an organic solvent solution.

[0018]Although the microemulsion containing the catalyst ultrafine particle produced by making it above can be used as catalytic liquid as it is, since this thing contains in production of composition of a carbon nanotube the surface-active agent which is not preferred, it is preferred to remove and use that surface-active agent. It distributes the catalyst phase again in a solvent, and let it be microemulsion, after carrying out centrifugal processing of the microemulsion, separating into a catalyst phase and a solvent phase and removal of the surface-active agent from microemulsion removing the solvent phase. Surfactant concentration obtains 0.1 or less % of the weight of catalytic liquid for such operation preferably 1 or less % of the weight multiple times and by usually repeating 3 to 5 times preferably 2 to 8 times. It is also possible to carry out extraction concentration of the catalyst ultrafine particle with the dialysis using the ultra filter as the other methods.

[0019]In the preparing method of other desirable catalytic liquid by this invention, Water-soluble catalyst metallic compounds are beforehand dissolved in water, it is considered as solution, this solution is distributed by the shape of an ultrafine particle in an organic solvent under existence of a surface-active agent, and it carries out by carrying out post-processing of the obtained microemulsion like the above. 0.05 mol/l. or less of concentration of the catalyst metallic compounds in solution is 0.02 mol/l. or less preferably, and although the lower limit in particular is not restrained, it is usually about 0.0001 mol/l.

[0020]In the above, although the catalyst metallic compounds which dissolve into liquid were returned and how to change into an insoluble metallic state was shown, it can replace with the reduction to the metal by this reduction, and the usual sedimentation method which makes precipitate of insoluble metallic compounds, such as metal hydroxide, a metallic oxide, metallic sulfide, generate can also be adopted.

[0021]Next, the catalytic liquid produced by making it above is made to dissolve thru/or distribute the photosensitive materials of the specified quantity. Desired coating liquid can be obtained by this.

[0022]Next, in this invention, said coating liquid is applied to a predetermined base, it dries and the photosensitive layer which consists of a catalyst and photosensitive materials is formed in the base surface. In this case, as that base, various kinds of publicly known things can be used conventionally. Although what is necessary is just a heat-resistant material of silicone, ceramics, stainless steel, etc., etc. as this base and it is not restrained in particular, what has a hydrophobic surface is preferred. In this invention, what has such a material on the surface at least is used. The shape of the base can be a sheet shaped, the shape of a board, a column,

tubed, etc. In this invention, a plate-like large area base can be used advantageously. This large area base is advantageously used as a catalyst substrate at the time of producing the electron source for field emission used for a planar display.

[0023]As a method of applying coating liquid on a base, various kinds of publicly known methods can be used conventionally. As such a method, the brush applying method, a roll coating method, a spray coating method, a spin coat method, the method of impregnating the base which carried out surface treatment, etc. are included.

[0024]Subsequently, negatives are developed after exposing to predetermined pattern state using the mask etc. which have a bore of pattern state to the photosensitive layer on the base produced by making it above. On the base, the pattern which consists of a catalyst and photosensitive materials is formed of this. In this case, that pattern can be a line, band-like, the shape of a lattice, dot form, and other arbitrary pattern state.

[0025]Development of the photosensitive layer exposed by said pattern state can be performed by the conventionally publicly known method of using the mixed liquor of water, an organic solvent, and water and an organic solvent, and other developing solutions. The proper method according to the photosensitive materials which use the concrete developing method is adopted.

[0026]Subsequently, the photosensitive materials included in it are removed from the pattern which consists of a catalyst formed on the base as mentioned above, and photosensitive materials. In this case, as a removing method of photosensitive materials, what is necessary is just the method of removing only those photosensitive materials without damaging a catalyst, and various kinds of methods can be used. As such a method, an elevated temperature and the method of usually calcinating at 700-900 ** preferably 500-1200 ** can be used in atmosphere [of oxidizing gases, such as the bottom of an inert gas atmosphere, air, oxygen gas,], or reducing gas atmosphere Shimo, such as hydrogen gas, etc. Thus, a predetermined catalyst pattern can be formed on a base.

[0027]In the catalyst pattern formed on the base, the state of the catalyst is just in the state of promoting generation of a carbon nanotube, and can be in the state of metallic boride, a metallic oxide, metallic sulfide, metal hydroxide besides a metallic state, etc. The coating weight of the catalyst ultrafine particle on a base is a rate of a 10^{-10} - 10^{-1} mol per 100-cm^2.

[0028]The catalyst pattern of this invention produced by making it above can be made to contain the catalyst support. In order to make the catalyst pattern containing catalyst support form, while making the catalyst metal which makes the solution which contains catalyst metal by a solution state contain catalyst support, and dissolves in it into this solution insolubilize with a hydrogen reduction method etc., it is made to deposit on catalyst support. Thus, coating liquid is made using catalytic liquid including the catalyst supported on the catalyst support formed, and a catalyst pattern is made as mentioned above using this coating liquid. As

catalyst support, various kinds of publicly known things are used conventionally. Various kinds of porous material, such as alumina, silica, silica alumina, magnesia, zirconia, boria, and zeolite, is included by such thing. 0.01-1 micrometer of the mean particle diameter is usually 0.05-0.5 micrometer preferably. The using rate is a rate of 0.1 to 10 weight section preferably 0.1 to 30 weight section per catalyst metal 100 weight section.

[0029]In other modes which manufacture the catalyst pattern of this invention, the coating liquid containing photosensitive materials and a catalyst precursor is prepared. In this case, although it depends on the kind of those photosensitive materials for the solvent which dissolves or distributes photosensitive materials, an aqueous solvent and an organic solvent are used. Although the concentration in particular of the photosensitive materials in coating liquid is not restrained, 10-1000 g/L is usually 100-500 g/L preferably. 10-500 g/L of catalyst precursor concentration is usually 20-100 g/L preferably. The rate of a catalyst precursor is a rate of one to 0. 5 weight section preferably 0.001 to 20 weight section per photosensitive-materials 100 weight section.

[0030]The catalyst precursor contained in coating liquid exists by a solution state in a solvent. Alcohol, ketone, ester, hydrocarbon, etc. are included as said organic solvent. As the example, for example Methanol, propyl alcohol, amyl alcohol, A hexanol, cyclohexanol, heptanol, octyl alcohol, cyclohexane, methyl ethyl ketone, a diethyl ketone, cycloheptane, n-hexane, n-heptane, isooctane, n-Deccan, benzene, toluene, xylene, etc. are mentioned. Use of the organic solvent which has the boiling point in the range which is 50-200 ** in this invention is preferred.

[0031]In order to prepare preferably the coating liquid containing said photosensitive materials and a catalyst precursor, catalyst precursor liquid is made, it ranks second and this catalyst precursor liquid is made to dissolve thru/or distribute photosensitive materials first in this invention. As a preparing method of catalyst precursor liquid, what is necessary is just a method which may dissolve a catalyst precursor uniformly into a solvent, and arbitrary methods can be used. The catalyst metallic compounds of fusibility are added to the solvent, and it is made to dissolve in it as a catalyst precursor to solvents, such as an organic solvent and water, first in the desirable preparing method. Thereby, catalyst precursor liquid is obtained.

[0032]In said catalyst precursor liquid, a surface-active agent can be added if needed. in this case -- as a surface-active agent -- an ionic surfactant -- a cationic surface-active agent and an anionic surface active agent are used preferably. The halogenides (a chloride, a bromide, etc.) of catalyst metal, organic acid salt (acetate etc.), organic complex salt (acetylacetonato, acetyl acetate, etc.), a nitrate, etc. are included by the soluble catalyst metallic compounds as said catalyst precursor.

[0033]Next, the catalyst precursor liquid produced by making it above is made to dissolve

thru/or distribute the photosensitive materials of the specified quantity. Desired coating liquid can be obtained by this.

[0034]Next, in this invention, said coating liquid is applied to a predetermined base, it dries and the photosensitive layer which consists of a catalyst precursor and photosensitive materials is formed in the base surface.

[0035]As a method of applying coating liquid on a base, various kinds of publicly known methods can be used conventionally. As such a method, the brush applying method, a roll coating method, a spray coating method, a spin coat method, the method of impregnating the substrate which carried out surface treatment, etc. are included.

[0036]Subsequently, negatives are developed after exposing to predetermined pattern state to the photosensitive layer on the base produced by making it above using a mask etc. On the base, the pattern which consists of a catalyst precursor and photosensitive materials is formed of this.

[0037]Development of the photosensitive layer exposed by said pattern state can be performed by the conventionally publicly known method of using the mixed liquor of water, an organic solvent, and water and an organic solvent, and other developing solutions. The proper method according to the photosensitive materials which use the concrete developing method is adopted.

[0038]Subsequently, while removing the photosensitive materials included in it from the pattern which consists of a catalyst precursor formed on the base as mentioned above, and photosensitive materials, a catalyst precursor is transformed to a catalyst. In this case, as the removing method of photosensitive materials, and a method of transforming a catalyst precursor to a catalyst, an elevated temperature and the method of usually calcinating at 700-900 ** preferably 500-1200 ** can be used by the inside of inactive gas, air, and oxygen gas, or the hydrogen gas middle class. Thus, a predetermined catalyst pattern can be formed on a base.

[0039]In said baking treatment, the catalyst pattern which consists of metallic oxides can be obtained by using oxidizing gas atmosphere and inert gas atmospheres, such as oxygen gas and air. By using reducing gas atmospheres, such as hydrogen gas and hydrogen-containing gas, the catalyst pattern which consists of metal of a metallic state can be obtained. By using the gas atmosphere containing hydrogen sulfide, the catalyst pattern which consists of metallic sulfide can be obtained. By using the atmosphere containing a boron compound, the catalyst pattern which consists of metallic borides can be obtained.

[0040]The catalyst pattern of this invention formed as mentioned above can be made to contain catalyst support. In order to form the catalyst pattern containing catalyst support, the catalyst precursor liquid which adds catalyst support in the catalyst precursor liquid which contains a catalyst precursor by a solution state, and contains this catalyst precursor and

catalyst support in it is made. Coating liquid is made using this catalyst precursor liquid, and a catalyst pattern is made as mentioned above using this coating liquid. As catalyst support, the above mentioned thing of **** various kinds is used.

[0041]In other methods of forming the catalyst pattern containing catalyst support, the catalyst precursor liquid which adds the catalyst support precursor of fusibility in the catalyst precursor liquid which contains a catalyst precursor by a solution state, and contains a catalyst support precursor in it by a solution state with a catalyst precursor is made. Coating liquid is made using this catalyst precursor liquid, and the pattern which consists of a mixture of a catalyst precursor, a catalyst support precursor, and photosensitive materials as mentioned above using this coating liquid is made. subsequently, this pattern -- the inside of oxidizing gas atmosphere, such as oxygen gas and air, and an inert gas atmosphere -- an elevated temperature -- 500-1200 ** is usually preferably calcinated at 700-900 **. Each of catalyst precursors and catalyst support precursors oxidizes, and the pattern which consists of a catalyst supported at catalyst support (porous metal oxide) is obtained by this calcination.

[0042]As said catalyst support precursor, soluble compounds, such as halogenides (a chloride, a bromide, etc.) of said catalyst support metal, organic acid salt (acetate etc.), organic complex salt, and nitrates (acetyl acetate, acetylacetonato, etc.), are used.

[0043]The catalyst pattern containing the catalyst support produced by making it above can obtain the catalyst pattern which consists of metal of a metallic state by calcinating this under reducing gas atmospheres, such as hydrogen gas and hydrogen-containing gas. By calcinating under the gas atmosphere containing hydrogen sulfide, the catalyst pattern which consists of metallic sulfide can be obtained. By calcinating under the atmosphere containing a boron compound, the catalyst pattern which consists of metallic borides can be obtained.

[0044]When calcinating the pattern which consists of a mixture of the above mentioned catalyst precursor and photosensitive materials under an inert gas atmosphere or oxidizing gas atmosphere, the removal process of the photosensitive materials from the pattern and the converting process to the catalyst of the catalyst precursor can be performed simultaneously. When calcinating the pattern which consists of a mixture of the above mentioned catalyst precursor, a catalyst support precursor, and photosensitive materials under an inert gas atmosphere or oxidizing gas atmosphere, The removal process of the photosensitive materials from the pattern, the converting process to the catalyst of the catalyst precursor, and the converting process to the catalyst support of the catalyst support precursor can be performed simultaneously.

[0045]As mentioned above, in this invention, although the removal process of the photosensitive materials from a pattern, and the catalyst of a catalyst precursor and/or a catalyst support precursor and/or the converting process to catalyst support can be performed simultaneously, it is not necessary to necessarily perform those processes simultaneously. For

example, after performing the removal process of photosensitive materials at low temperature using low-temperature oxygen plasma etc. first, it can calcinate at an elevated temperature under an oxidizing atmosphere, and the catalyst precursor and/or a catalyst support precursor can be transformed to a catalyst and/or catalyst support.

[0046]The catalyst pattern of this invention is excellent in the resolution, and small-gage wire width can obtain a catalyst pattern of 10 micrometers or less.

[0047]Although activity energy lines, such as ultraviolet rays and an electron beam (electron beam), are included by the light used by an exposure process in this invention, in a actual exposure process, a proper thing is selected according to the characteristic of the photosensitive materials to be used.

[0048]In order to manufacture a carbon nanotube using the catalyst pattern of this invention, the pyrolysis of the carbon-containing material is carried out by the shape of a gas under existence of the catalyst pattern.

[0049]The carbon-containing material in particular used by this invention is not restrained, but should just be carbonized at an elevated temperature. As such a thing, ethane, methane, propane besides carbon monoxide, Saturated hydrocarbon, such as butane; aromatic hydrocarbon, such as acetylene series compound; benzene, such as unsaturated hydrocarbon; acetylene, such as ethylene, propylene, a butene, and isobutene, toluene, xylene, and naphthalene, these mixtures (for example, naphtha, gas oil, etc.), etc. are included. In this invention, use of the organic carbon material from points, such as an ease of handling, a point of a price, carbon content, and liquefied aromatic hydrocarbon whose boiling point is 80-144 ** especially, for example, BENZERU, toluene, xylene, and those mixtures is preferred.

[0050]As the method of carrying out the pyrolysis of the carbon-containing material, a publicly known method is used conventionally. The usual heating method by an electric furnace etc., the heating method by microwave, the laser-heating method, etc. are included by such method. In the case of the usual heating method, 600-1000 ** of the cooking temperature is 700-900 ** preferably. When carrying out the pyrolysis of said carbon-containing material, hydrogen gas can be mixed as carrier gas into the gas of the carbon-containing material. A proper quantity of sulfur compounds, such as hydrogen sulfide and mercaptan, can be added to carbon-containing material. Thereby, a straight carbon nanotube can be obtained on a substrate.

[0051]When making a carbon nanotube generate as mentioned above using the catalyst pattern of this invention, a carbon nanotube is formed along the catalyst pattern top, and a carbon nanotube pattern is formed on a base.

[0052]

[Example]Next, this invention is further explained in full detail according to an example.

[0053]As a preparation catalyst support precursor of Example 1 (1) coating liquid, the aluminum ($AlCl_3$and6H_2O) to the methanol solution which melted 80 g/L and chloridation Silang ($SiCl_4$) by the concentration of 56 g/L as a catalyst precursor, The catalyst precursor liquid which contains a catalyst support precursor by a solution state with a catalyst precursor was prepared by adding 10.8 g/L and a molybdenum chloride ($MoCl_5$) so that it may become the concentration of 0.3 g/L, and dissolving ferric chloride 6 hydrate ($FeCl_3$and6H_2O). Next, in addition to the anisole solution 0.1L which contains the polymethylmethacrylate (PMMA) of electron beam photosensitivity by the concentration of 50 g/L as photosensitive materials of a negative mold, this catalyst precursor liquid 0.1L was mixed uniformly ultrasonically, and coating liquid was prepared.

(2) On the formation silicone groups board of a photosensitive layer, the spin coat of the coating liquid of the above (1) was carried out, it dried and the coat (photosensitive layer) about 0.5 micrometer thick was formed. This coat consists of a mixture of the ferric chloride as a catalyst precursor and a molybdenum chloride, the aluminium chloride as a catalyst support precursor, chloridation Silang, and the polymethylmethacrylate (PMMA) as photosensitive materials.

(3) The exposure exposure of the electron beam was carried out to the photosensitive layer formed on the silicone groups board obtained with the pattern state exposure above (2) of the photosensitive layer from electron beam irradiation equipment (the Elionix, Inc. make, product name "ELS-7300").

(4) Negatives were developed by immersing the exposure photosensitive layer obtained with the development above (3) of the photosensitive layer for about 1 minute at a room temperature into the mixed liquor of methyl isobutyl ketone and isopropyl alcohol. Elution removal of the unexposed part coat was carried out by this development, and the resin pattern containing the catalyst precursor and catalyst support precursor corresponding to a pattern of a mask was obtained.

(5) The resin pattern obtained with the formation above (4) of the catalyst pattern supported by catalyst support was put in in the electric furnace, and temperature up was carried out to 900 ** under argon atmosphere. Thereby, it is a catalyst in the fine pores of the network of alumina and silicon oxide. [Iron oxide (FeOx) and oxidation molybdenum (MoOx]) The catalyst pattern to contain was obtained.

[0054](6) In the manufacture above (5) of a carbon nanotube pattern, the temperature of 900 ** was held after formation of the catalyst pattern, the mixed gas which consists of methane 20% and argon 80% was passed, and the carbon nanotube was formed in pattern state along with the catalyst pattern in methane. In this carbon nanotube pattern, the minimum width of that small-gage wire is 0.02 micrometer, the least interval between small-gage wires is 0.02

micrometer, and the high resolution pattern was obtained.

[0055]In example 2 Example 1, while using the xylene solution containing UV photosensitivity resin (the Clariant, LTD. make, product name "AZ1350") of a positive type as a solution containing photosensitive materials, it experimented similarly except having used the black light (made by Mikasa, Inc) instead of electron beam irradiation equipment. As a result, the exposure part became blank in this case, and the carbon nanotube pattern which excelled [non-exposed area] in the resolution which remains in pattern state was manufactured.

[0056]In preparation methanol of Example 3 (1) coating liquid, an alumina particle (mean particle diameter: 0.1 micrometer) 120 g/L, In addition to the anisole solution 0.1L which contains PMMA by the concentration of 50 g/L, the catalyst precursor liquid 0.1L which contains 60 g/L and molybdenum acetyl acetate for iron nitrate (II) by the concentration of 30 g/L was mixed uniformly ultrasonically, and coating liquid was prepared. It experimented like Example 1 except having used this coating liquid. As a result, the carbon nanotube pattern was manufactured along the catalyst pattern top which consists of oxidation mol BITEN which consists of the iron oxide and oxidation molybdenum which were supported by alumina support.

[0057]In the preparation toluene 9g of Example 4 (1) catalytic liquid, 1g of didecyl dimethylannmonium star's pictures (DDAB) which are a cationic surface-active agent are melted, and are stirred for 1 hour. Next, 12 mg of cobalt chloride 6 hydrates are introduced into a solution, and are stirred for further 1 hour. This solution shows a transparent light blue. Then, 15micro of sodium borohydride solution of 10M is dropped I times, and a cobalt chloride is returned. After dropping, a solution is suspended black and produces the sediment of silver gray. Next, after covering the solution containing this sediment over an at-long-intervals heart separator at 12000 rpm for 10 minutes and removing a supernatant fluid, re dispersion of the toluene is added and carried out, by repeating the process of carrying out centrifugal processing, 4 times, an excessive surface-active agent is removed and a cobalt particle is refined. Thus, in the obtained catalytic liquid, the mean particle diameter of the cobalt particle is about 4 nm. The surfactant concentration is less than zero %1wt% on parenchyma. In addition to the anisole solution 0.1L which contains PMMA by the concentration of 50 g/L, the catalytic liquid 0.1L of the above (1) was mixed uniformly ultrasonically, and coating liquid was prepared. It experimented like Example 1 except having used this coating liquid. As a result, the carbon nanotube pattern was manufactured along the catalyst pattern top which consists of cobalt.

[0058]

[Effect of the Invention]According to this invention, a complicated catalyst pattern with sufficient resolution can be manufactured easily. And a carbon nanotube pattern can be manufactured with sufficient resolution along that catalyst pattern top by performing the pyrolysis of carbon-

containing material on this catalyst pattern. A various application is presented with the carbon nanotube pattern obtained by this invention according to the shape of the pattern.

[Translation done.]